

MELTING AND DIFFUSIONAL SOLIDIFICATION BEHAVIOUR OF TLP SINTERED POWDERS:

AN *in situ* NEUTRON DIFFRACTION STUDY

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INTRODUCTION

In transient liquid phase sintering (TLPS) processes, powder mixtures/compacts typically consist of a low melting point additive phase and a higher melting point base metal (Cu and Ni powders respectively in this case). During the sintering cycle, the mixture is partially liquated by heating to an isothermal process temperature (T_P) above the additive's melting point yet below that of the base metal. By holding the mixture at T_P , the transient liquid phase can be gradually removed isothermally via diffusional solidification processes by interaction with the base metal (e.g., solute diffusion from the liquid into the solid base metal powder particle) (1). The amount and duration of the liquid phase, which are difficult to accurately measure, have been found to significantly affect the degree of densification achieved during the process (2). Previous differential scanning calorimetry results (3) have permitted the quantification of the amount of liquid initially formed as well as its rate of removal. However, the interdiffusion processes responsible for isothermal solidification are not well understood due to the lack of appropriate *in situ* data. Fischer and Rudman (4) and Delhez *et al* (5) have shown that *ex situ* x-ray diffraction analysis can provide valuable insight regarding additive/base interdiffusion for solid-state sintered powder mixtures in the absence liquid. The objectives of this *in situ* neutron diffraction study are to investigate the impact of interdiffusion on the melting event in TLPS as well as the isothermal/diffusional solidification process at various T_P above the Cu melting point.

MATERIALS AND METHODS

Elemental Ni and Cu powders (bulk mixture composition, $C_O = 65$ wt.% Cu) were mixed and then sintered in large cylindrical Al_2O_3 crucibles (6mm \varnothing , 42mm tall), within the C2 powder diffractometer located at the NRU research reactor at the Chalk River Labs (Chalk River, Canada). A planar Si single crystal was used to generate a monochromatic incident beam ($\lambda = 1.33069$ Å). Sequential diffraction patterns were collected at one minute intervals during the sintering cycles (0.1° step size spanning 20-100° in 2θ). Multiple sintering experiments were conducted by linearly heating at 40 °C/min. and holding at various peak temperatures (T_P) above the Cu melting point (i.e., 1085-1200 °C) in 99.998% N_2 . ND patterns were analyzed using GSAS code and Powder3D®, which facilitates the interpretation of large ND data arrays.

RESULTS AND ANALYSIS

Fig. 1 presents a Powder3D® plot showing intensity contrast in the 40-50° range for 990 sequential diffraction patterns (data sets along ordinate axis) collected at one minute intervals during heat-up and isothermal sintering at $T_P = 1140$ °C. The high-temperature pure (200) Ni and Cu reflections as well as the Al_2O_3 crucible reflections are shown. Since Cu and Ni are completely soluble, a continuous linear variation of alloy lattice parameters can form; therefore the 2θ axis is analogous to composition. During the initial heat-up datasets, all reflections shift to lower angles due to thermal expansion of the respective lattices. Once the isothermal processing temperature is reached, the inert Al_2O_3 peak positions stabilize and these serve as useful, internal temperature references. The Cu (200) peak is abruptly removed from the diffraction pattern due to Cu powder melting at 1085 °C, whereas the Ni peak continues to shift moderately and temporarily stabilize at T_P . Prolonged sintering at 1140 °C for over 900 min. shows the eventual formation of a broader single peak at

intermediate angles between pure Cu and Ni, which agrees well with that expected for a fully solidified homogeneous alloy (i.e., $C_O = 65\%$ Cu). Immediately following the melting event however, a Cu-rich peak begins to form - hereafter referred to as the solidus, or 'C_S', peak. This peak's intensity grows rapidly, thus indicating the rapid post-melt growth of Cu-rich solid-solution regions surrounding Ni-rich particle cores, as metallographically observed in (3).

In brief, similar experiments were completed at various T_P and the C_S peak positions were tracked immediately after the melting event prior to complete liquid removal. The corresponding Cu-Ni alloy compositions were determined from the post-melt C_S peak positions for each experiment. Fig. 2 shows that the compositions indicated by the C_S ND peaks are coincident with the Cu-Ni solidus. These *in situ* results confirm that the transient liquid is primarily removed by the rapid epitaxial growth of a Cu-rich solid solution 'shell' (at a composition given by the solidus) surrounding the Ni-rich base metal particles.

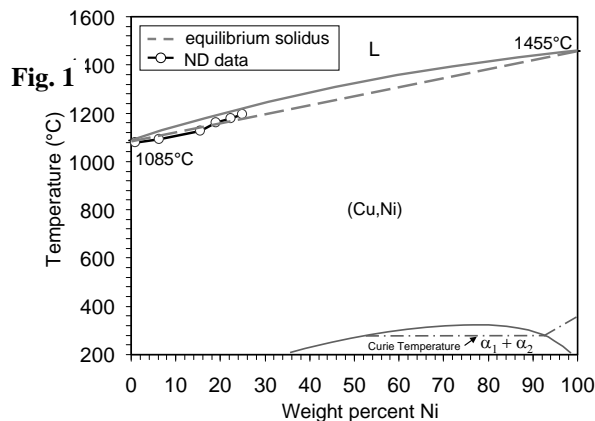
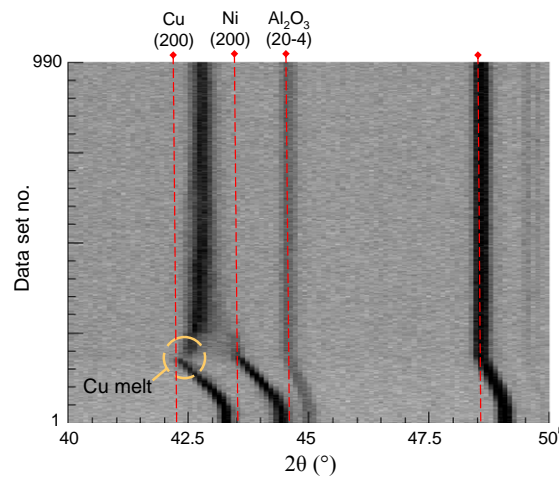


Fig. 1

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